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(72) Jandel, Lothar, DE

(72) Krause, Siegfried, DE

(72) Rademacher, Josef, DE

(73) PPG INDUSTRIES, INC., US

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(54) **VERNIS EN POUDRE ET SON UTILISATION DANS LE
REVETEMENT DE L'INTERIEUR DE CONTENANTS
D'EMBALLAGE ET LE RECOUVREMENT DE CORDONS DE
SOUDURE**

(54) **POWDERED VARNISH AND ITS USE FOR COATING THE
INSIDES OF PACKAGING CONTAINERS AND FOR
COVERING WELD SEAMS**

(57) The object of the invention is a powdered varnish which: 1) contains at least one polyester with an acid number of 25 to 120 mgKOH/g and an OH number > 10 mgKOH/g and at least one epoxy resin with an epoxy equivalent weight of 400 to 3000; 2) for covering weld seams has such a grain size distribution that at least 90 % mass of the powdered varnish particles have a particle size between 1 and 100 μm , the maximum particle-size of the powdered varnish particles is $\leq 150 \mu\text{m}$, the average size of the powdered varnish particles lies between > 20 and 60 μm and the gradient of the grain distribution curve at the knee is > 50, or 3) for the internal coating of packaging containers has such a grain sized distribution that at least 90 % mass of the powdered varnish particles have a particle size of between 1 and 60 μm , the maximum size of the powdered varnish particles is $\leq 100 \mu\text{m}$, the average size of the powdered varnish particles lies between 5 and 20 μm and the gradient of the grain distribution curve at the knee is > 100.




PCT

WELTORGANISATION FÜR GEISTIGES EIGENTUM
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INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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<p>(21) Internationales Aktenzeichen: PCT/EP91/02099 (22) Internationales Anmeldedatum: 6. November 1991 (06.11.91) (30) Prioritätsdaten: P 40 38 681.3 5. Dezember 1990 (05.12.90) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF LACKE + FARBEN AKTIENGESELLSCHAFT (DE/DE); Max-Winkelmann-Straße 80, D-4400 Münster (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): JANDEL, Lothar (DE/DE); Linckensstraße 33, D-4400 Münster (DE). KRAUSE, Siegfried (DE/DE); Auf der Woort 19, D-4400 Münster (DE). RADEMACHER, Josef (DE/DE); Linckensstraße 117, D-4400 Münster (DE).</p>		<p>(74) Anwalt: LEIFERT, Elmar; BASF Lacke + Farben AG, Postfach 61 23, D-4400 Münster (DE). (81) Bestimmungsstaaten: AT (europäisches Patent), BE (europäisches Patent), BR, CA, CH (europäisches Patent), DE (europäisches Patent), DK (europäisches Patent), ES (europäisches Patent), FR (europäisches Patent), GB (europäisches Patent), GR (europäisches Patent), IT (europäisches Patent), LU (europäisches Patent), NL (europäisches Patent), NO, SE (europäisches Patent), US. Veröffentlicht Mit internationalem Recherchenbericht.</p>
<p>(54) Title: POWDERED VARNISH AND ITS USE FOR COATING THE INSIDES OF PACKAGING CONTAINERS AND FOR COVERING WELD SEAMS (54) Bezeichnung: PULVERLACK UND DESSEN VERWENDUNG ZUR INNENBESCHICHTUNG VON VERPAKUNGSBEHÄLTERN UND ZUR SCHWEISSNAHTABDECKUNG (57) Abstract  The object of the invention is a powdered varnish which: 1) contains at least one polyester with an acid number of 25 to 120 mgKOH/g and an OH number > 10 mgKOH/g and at least one epoxy resin with an epoxy equivalent weight of 400 to 3000; 2) for covering weld seams has such a grain size distribution that at least 90 % mass of the powdered varnish particles have a particle size between 1 and 100 µm, the maximum particle size of the powdered varnish particles is ≤ 150 µm, the average size of the powdered varnish particles lies between > 20 and 60 µm and the gradient of the grain distribution curve at the knee is > 50, or 3) for the internal coating of packaging containers has such a grain sized distribution that at least 90 % mass of the powdered varnish particles have a particle size of between 1 and 60 µm, the maximum size of the powdered varnish particles is ≤ 100 µm, the average size of the powdered varnish particles lies between 5 and 20 µm and the gradient of the grain distribution curve at the knee is > 100. (57) Zusammenfassung Gegenstand der vorliegenden Erfindung ist ein Pulverlack, der dadurch gekennzeichnet ist, dass er 1) mindestens einen Polyester mit einer Säurezahl von 25 bis 120 mgKOH/g und einer OH-Zahl > 10 mgKOH/g und mindestens ein Epoxidharz mit einem Epoxidäquivalentgewicht von 400 bis 3000 enthält, 2) für die Schweissnahtabdeckung eine derartige Korngrößenverteilung aufweist, dass mindestens 90 Massenprozent der Pulverlackteilchen eine Teilchengröße zwischen 1 und 100 µm aufweisen, die maximale Teilchengröße der Pulverlackteilchen ≤ 150 µm beträgt, die mittlere Teilchengröße der Pulverlackteilchen zwischen > 20 und 60 µm liegt und die Steilheit der Kornverteilungskurve am Wendepunkt > 50 ist oder 3) für die Innenbeschichtung von Verpackungsbehältern eine derartige Korngrößenverteilung aufweist, dass mindestens 90 Massenprozent der Pulverlackteilchen eine Teilchengröße zwischen 1 und 60 µm aufweisen, die maximale Teilchengröße der Pulverlackteilchen ≤ 100 µm beträgt, die mittlere Teilchengröße der Pulverlackteilchen zwischen 5 und 20 µm liegt und die Steilheit der Kornverteilungskurve am Wendepunkt > 100 ist.</p>		

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BASF Lacke + Farben Aktiengesellschaft, Münster

5 Powder coating and the use thereof for the coating of
 packaging container interiors and of weld seams

 The present invention relates to powder coatings, based
 on epoxy resins and carboxyl-containing polyesters, for
 the coating of packaging container interiors and weld
10 seams. In addition, the present invention relates to the
 process of coating packaging container interiors and weld
 seams as well as to the use of the powder coatings.

 Packaging containers, such as food cans, two- and three-
 part beverage cans and others, are provided on the inside
15 with a coating, the purpose of which is on the one hand
 to protect the contents from contamination by dissolved
 constituents of the metal sheeting and on the other hand
 to prevent corrosion of the metal sheeting by aggressive
 contents.

20 This coating of the packaging containers takes place in
 practice mainly by means of organically dissolved
 coatings. However, this causes high solvent
 contamination of the environment on drying of the coating
 films. Attempts have therefore been increasingly made to

replace these coatings by low-solvent or solvent-free coatings. Thus, for example, thermoplastic powder coatings have frequently been used to coat can weld seams. These products are produced from the
5 corresponding thermoplastics by an expensive cold grinding process.

Furthermore, thermosetting powder coatings for the coating of weld seams of metal containers used for foodstuffs or beverages are known from EP-B-119,164.
10 These thermosetting powder coatings contain, as binder, a mixture of an aromatic epoxy resin having on average not more than 2 epoxide groups per molecule, and an aromatic epoxy resin having on average more than 2 epoxide groups per molecule. The condensation product
15 of bisphenol A diglycidyl ether with bisphenol A and/or an acid polyester based on trimellitic anhydride/aliphatic polyol is used as curing agent. However, EP-B-119,164 contains no information on suitable particle sizes and particle size distribution of the
20 powder coatings. In addition, it is a drawback that these powder coatings are only suitable for the coating of weld seams.

Powder coatings for the coating of can interiors, which contain a polyester having terminal carboxyl groups and
25 an OH value lower than 10 mg of KOH/g as well as an epoxy resin, are known from EP-B-10,805. These powder coatings contain choline derivatives as curing catalyst. The

powder coatings have an average particle size between 20 and 150 μm . However, EP-B-10,805 contains no information on how to obtain can interior coatings which would provide closed films even at film thicknesses of $\leq 15 \mu\text{m}$.
5 Furthermore, owing to the low OH value of the polyester, these powder coatings have the drawback of having only poor crosslinking. Correspondingly, this system has drying times of 10 to 40 min. at 150 to 220°C which are unacceptable in practice, while the drying time in
10 modern production lines is not more than 20 to 30 sec. at an object temperature of 260 to 280°C.

Powder coatings for the coating of can interiors and can lids which contain an epoxy resin and aromatic amines, Lewis acids and acid anhydrides as curing agents, are
15 known from US Patent 4,497,837. The powder coatings have an average particle size between 20 and 150 μm , preferably 30 to 70 μm . The drawback of these systems is the high minimum film thickness of 38 μm for obtaining coatings which are not excessively porous. Moreover,
20 these powder coatings have the drawback of oven dwell times between 5 and 12 min. being required for the curing of the systems described.

Furthermore, powder coatings which also contain an epoxy resin and aromatic amines, epoxide-amine adducts or acid
25 anhydrides, for the coating of can interiors are known from US Patent 3,962,486. By using the plasma spray coating process it is possible to produce coatings which,

at low film thicknesses of less than 13 μm , comply with the requirements which are usually specified for interior coatings of foodstuff containers. To ensure applicability by the plasma spray process, only those powder coatings which have a maximum particle size of $\leq 100 \mu\text{m}$ and a sufficiently low melt viscosity should be used.

However, the use of aminic curing agents leads to an inadequate resistance to sterilization of the resultant coatings. It is furthermore a drawback that amine-cured epoxy resins tend to be brittle and have very poor flexibility. Acid anhydride curing agents have the disadvantage of being strongly irritant, thus requiring special protective measures in the formulation of the powder coatings.

Finally, powder coatings for the coating of can interiors which contain an epoxy resin and an amine curing agent, are known from US Patent 4,183,974. These powder coatings have an average particle size between 1 and 100 μm , preferably between 1 and 10 μm . It is true that the resultant coatings have the required low porosity at film thicknesses as low as $\leq 13 \mu\text{m}$, but the resistance to sterilization of the resultant coatings is in the need of improvement. Furthermore, it is a drawback that amine-cured epoxy resins tend to be brittle and have very poor flexibility.

The object of the present invention is to make available powder coatings which, with the same chemical composition, are suitable both for weld seam coating and for the coating of packaging container interiors, in particular metal container interiors. In addition, these powder coatings, when used for the coating of packaging container interiors and when applied at film thicknesses as low as $\leq 15 \mu\text{m}$, should comply with the requirements which are usually specified for can interior coatings. In particular, these interior coatings should not be porous (determined with the aid of a so-called enamel rater test), they should possess good adhesion to the substrate and good flexibility, and they should withstand the customary pasteurization and sterilization conditions. Furthermore, these powder coatings, when used for weld seam coating, should lead to highly flexible coatings which withstand the mechanical deformations incurred in the flanging and of the cans beading. Resistance to sterilization and pasteurization is also required after the deformative treatment.

The powder coatings should be curable in the course of the brief drying times which are customary in can coating.

Surprisingly, this object is achieved by a powder coating of the type referred to at the outset, wherein

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1.) the powder coating contains

A) at least one polyester having an acid value of 25 to 120 mg of KOH/g and an OH value \geq 10 mg of KOH/g and

5 B) at least one epoxy resin having an epoxide equivalent weight of 400 to 3000, and

2.) the powder coating has such a particle size distribution that

10 a) at least 90% by mass of the powder coating particles have a particle size between 1 and 60 μm ,

b) the maximum particle size for at least 99% by mass of the powder coating particles is \leq 100 μm ,

15 c) the average particle size of the powder coating particles is between 5 and 20 μm , and

d) the slope of the particle distribution curve at the inflection point is greater than or equal to 100.

20 Furthermore, the invention relates to a powder coating for the coating of packaging contain r weld seams based on epoxy resins and carboxyl-containing polyesters,

wherein

1.) the powder coating contains

- A) at least one polyester having an acid value of 25 to 120 mg of KOH/g and an OH value of ≥ 10 mg of KOH/g, and
- B) at least one epoxy resin having an epoxide equivalent weight of 400 to 3000, and

10

2.) the powder coating has such a particle size distribution that

- a) at least 90% by mass of the powder coating particles have a particle size between 1 and 100 μm ,
- b) the maximum particle size for at least 99% by mass of the powder coating particles is $\leq 150 \mu\text{m}$,
- c) the average particle size of the powder coating particles is between > 20 and $60 \mu\text{m}$, and

20

- d) the slope of the particle distribution curve at
the inflection point is ≥ 50 .

In addition, the invention relates to processes for the coating
of packaging container interiors and weld seams

in which these powder coatings are applied. The invention finally also relates to the use of the powder coatings for the coating of packaging container interiors and weld seams.

5 It is surprising, and could not have been foreseen, that the powder coatings according to the invention are suitable, with the same chemical composition, for the coating both of weld seams and of packaging container interiors and that the property profile and hence the use can be regulated simply by establishing a corresponding
10 particle size distribution. At the same time these powder coatings are rapidly curable, simple to handle and simple to apply.

Furthermore, the powder coatings according to the invention, when used for the coating of packaging container
15 interiors, are distinguished by the fact that coatings with a very low film thickness of only $\leq 15 \mu\text{m}$ possess the properties required by can manufacturers. In particular, these coatings have the required low porosity at a film thickness as low as $\leq 15 \mu\text{m}$. Moreover, these
20 coatings possess good adhesion, high flexibility and good resistance to pasteurization and sterilization.

Furthermore, the powder coatings according to the invention, when used for weld seam coating, have the advantage of high flexibility, with the result that the weld seam
25 coating is able to follow the deformations of the packaging container on further fabrication without peeling off

or cracking. Moreover, it is an advantage that, in contrast in aminic curing agents, the powder coating according to the invention attains good resistance to sterilization.

The individual components of the powder coatings according to the invention are now elucidated in greater detail below. The polyesters employed in the powder coatings according to the invention (component A) have an acid value of 25 to 120 mg of KOH/g, preferably 30 to 90 mg of KOH/g and particularly preferably 60 to 90 mg of KOH/g, and an OH value of at least 10
10 mg of KOH/g, preferably at least 15 mg of KOH/g and preferably lower than or equal to 30 mg of KOH/g. Polyesters having a functionality of ≥ 2 are preferably employed. The number average molecular weights of the polyesters are generally between 1000 and 10,000, preferably between 1500 and 5000. Polyesters approved by the US FDA (FDA = Food and Drug Administration) are preferably used. The carboxyl- and hydroxyl-containing polyesters can be prepared by conventional methods (cf., for example, Houben Weyl, Methoden der organischen Chemie, [Methods of Organic Chemistry], 4th edition, volume 14/2, Georg Thieme
20 Verlag, Stuttgart 1961.)

Aliphatic, cycloaliphatic and aromatic dicarboxylic and polycarboxylic acids, such as phthalic acid, terephthalic acid, isophthalic acid, trimellitic acid, pyromellitic acid, adipic acid, succinic acid, glutaric acid, pimelic

acid, suberic acid, acelaic acid, sebacic acid and others, are suitable as the carboxylic acid component in the preparation of the polyesters. The acids can also be used in the form of their derivatives capable of esterification (for example anhydrides) or transesterification (for example dimethyl esters).

The commonly used diols and/or polyols, for example ethylene glycol, 1,2- and 1,3-propanediol, butanediols, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolpropane, diglycerol and others, are suitable as the alcohol component in the preparation of the polyesters. The polyesters obtained in this manner can be used either individually or as a mixture of different polyesters.

Any solid epoxy resin having an epoxide equivalent weight between 400 and 3000, preferably between 600 and 900 and particularly preferably between 700 and 800, is suitable as the component B. Epoxy resins based on bisphenol A and/or epoxidized novolak resins are preferably used. The epoxy resins based on bisphenol A generally have a functionality ≤ 2 , and the epoxidized novolak resins a functionality of ≥ 2 .

Examples of suitable epoxy resins are products commercially available under the following names: Epikote® 154,

1001, 1002, 1055, 1004, 1007, 1009, 3003-4F-10 from Shell
Chemie, XZ 86 795* and DER* 664, 667, 669, 662, 642U and 672U
from Dow and Araldite* XB 4393, XB 4412, GT 7072, GT 7203, GT
7004, GT 7304, GT 7097 and GT 7220 from Ciba Geigy.

Epoxy resins approved by the FDA are preferably employed.

The polyester component A is normally used in an amount of 19 to
80 % by weight, preferably of 39 to 60 % by weight, based on the
10 total weight of the powder coating. The epoxy resin component B
is normally used in an amount of 19 to 80 % by weight,
preferably of 39 to 60 % by weight, based on the total weight of
the powder coating.

As a further component C, the powder coatings according to the
invention contain at least one curing catalyst, normally used in
an amount of 0.01 to 5.0 % by weight, preferably of 0.05 to 2.0
% by weight, in each case based on the total weight of the
powder coating.

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The catalyst used is preferably imidazole, 2-methylimidazole,
ethyltriphenylphosphonium chloride or another salt of the same
compound, a quinoline derivative, such as that described in

*Trade-mark

EP-B-10,805, a primary, secondary or tertiary aminophenol, aluminum acetylacetonate or a salt of toluenesulfonic acid or a mixture of different catalysts listed above.

The carboxyl- and hydroxyl-containing polyester resins available commercially usually already contain the required curing catalyst. Examples of such carboxyl- and hydroxyl-containing polyesters available commercially which are particularly preferably used are the products available commercially under
10 the following brand names: Crylcoat* 314, 340, 344, 2680, 316, 2625, 320, 342 and 2532 from UCB, Drogenbos, Belgium, Grilesta* 7205, 7215, 72-06, 72-08, 72-13, 72-14, 73-72, 73-93 and 7401 from Ems-Chemie and Neocrest* P 670, P 671, P 672, P 678 and P 662* from ICI.

In addition, the powder coatings according to the invention may also contain 0 to 40 % by weight, preferably 15 to 25 % by weight, of fillers (component D). Fillers approved by the FDA are preferably used. In general, inorganic fillers, for example
20 titanium dioxide such as Kronos* 2160 from Kronos Titan, rutile R 902 from Du Pont and RC 566 from Sachtleben, barium sulfate and silicate-based fillers, such as talc, kaolin, magnesium aluminum silicates, mica and others are used. Titanium dioxide and fillers of the quartz sand type are preferably used.

*Trade-mark

Furthermore, the powder coatings according to the invention may also contain, where appropriate, 0.01 to 10 % by weight, preferably 0.1 to 2 % by weight, based on the total weight of the powder coating, of other auxiliary substances and additives. Examples of these are flow control agents, spraying agents, deaeration agents, such

as benzoin, pigments and others.

The preparation of the powder coatings is performed by known methods (cf., for example, product information from BASF Lacke + Farben AG, "Pulverlacke", ["Powder Coatings"], 1990) by homogenization and dispersion, for example by means of an extruder, worm kneader and others. It is an essential part of the invention that the particle size distribution of the powder coatings, following their preparation, is adjusted to suit the application by grinding and, if appropriate, by screening and sieving.

For use in the coating of packaging container interiors, the particle size distribution (a) is adjusted in such a way that at least 90 % by mass of the powder coating particles have a particle size between 1 and 60 μm , i.e. $d_{90} = 1$ to 60 μm . Preferably 90 % by mass of the powder coating particles have a particle size between 1 and 40 μm ($d_{90} = 1$ to 40 μm) and particularly preferably between 5 and 25 μm ($d_{90} = 5$ to 25 μm). For at least 99 % by mass of the particles, the maximum particle size of the powder coating particles is $\leq 100 \mu\text{m}$, preferably $\leq 60 \mu\text{m}$ and particularly preferably $\leq 40 \mu\text{m}$). The average particle size of the powder coating particles is between 5 and 20 μm , particularly preferably between 5 and 12 μm . Furthermore, it is an essential part of the invention that, when the powder coatings are used for the coating of packaging container interiors, the particle size distribution is adjusted in such a way that the

slope S of the particle distribution curve at the inflection point is ≥ 100 , preferably ≥ 150 and particularly preferably ≥ 200 . To obtain coatings having particularly good properties, it is most particularly preferred to use powder coatings in which the slope S of the particle distribution curve at the inflection point is ≥ 300 . However, the production costs of powder coatings increase considerably with increasing slope. The slope S is defined as limit value for

10 $f(x_2) - f(x_1)$ against zero of $(f(x_2) - f(x_1))/\lg((x_2/x_1))$ at the inflection point of the particle distribution curve. The particle distribution curve thus represents the plot of the accumulated percentages by mass against the absolute particle diameter (represented logarith-

15 mically). Accordingly, for use in the coating of packaging container interiors, suitable powder coatings are in particular those which contain only a small proportion of very fine particles (particle size $< 5 \mu\text{m}$) and also a very small proportion of coarse powder coating

20 particles (particle size $> 25 \mu\text{m}$), i.e. they have as narrow a particle size distribution as possible.

For use in the coating of weld seams, the particle size distribution (b) is adjusted in such a way that at least 90 % by mass of the powder coating particles have a

25 particle size between 1 and $100 \mu\text{m}$. Preferred powder coatings are those in which at least 90 % by mass of the powder coating particles have a particle size between 5 and $100 \mu\text{m}$. In this case the slope S , defined above, of

the particle distribution curve at the inflection point can also be below 100. The slope is usually ≥ 50 , preferably > 100 . For at least 99 % by mass of the particles, the maximum particle size of the powder coating particles is $\leq 150 \mu\text{m}$, preferably $\leq 100 \mu\text{m}$. The average particle size of the powder coating particles is preferably between > 20 and $60 \mu\text{m}$, particularly preferably between 25 and $40 \mu\text{m}$.

Accordingly, the powder coatings used for the coating of packaging container interiors are in principle also suitable for use in the coating of weld seams. However, powder coatings preferred for use in the coating of weld seams are those which contain a high proportion of coarse powder coating particles.

The adjustment of the particle size distribution of the powder coatings is carried out in each case with the aid of suitable grinding aggregates, if appropriate in combination with suitable screening and sieving equipment, e.g. using a fluidized bed opposed jet mill (AFG) from Alpine, Augsburg, in combination with an ultra-fine classifier from Alpine, Augsburg.

The packaging containers which are coated with the powder coatings according to the invention, can be made of a variety of materials, can be of a variety of sizes and shapes and can be produced by various processes. However, metal containers in particular are coated by the powder coatings according to the invention. These metal containers can be prepared by first rolling and then

folding back the metal plate. The end pieces can then be affixed to the cylinder produced in this way. The powder coatings according to the invention are used for the coating of the weld seam as well as for the coating of the can body interiors, which generally are already provided with a bottom. In addition, the interiors of deep-drawn metal containers can also be coated with the powder coatings according to the invention. The powder coatings are of course also suitable for the coating of can lids and can bottoms.

The packaging containers can be made from a variety of materials, such as aluminum, black plate, tin plate, and various ferrous alloys which are provided, if necessary, with a passivation coat based on nickel, chromium and tin compounds.

Containers of this type are usually used as containers for foodstuffs and beverages, such as beer, juices, fizzy drinks, soups, vegetables, meat dishes, fish dishes, vegetables, but also, for example, for pet foods. Application is carried out by known methods, for example those described in US Patent 4,183,974. The electrostatic charging of the powder coating particles is carried out by friction (triboelectricity). Application of the powder coating particles is performed with the aid of special spray heads, known to a person skilled in the art.

For the coating of packaging container interiors, the powder coatings are normally applied at a film thickness of $\leq 15 \mu\text{m}$, preferably of 10 to $14 \mu\text{m}$. Even at these low film thicknesses, the coatings comply with the requirements normally specified for such films. The powder coatings can of course also be applied in higher film thicknesses. For the coating of weld seams, the powder coatings are normally applied at a film thickness of $\leq 200 \mu\text{m}$, preferably $\leq 80 \mu\text{m}$. The packaging containers whose weld seam or interior have been coated with the powder coating according to the invention, are subsequently heat-treated in order to cure the powder coating. This heat treatment can be performed in a variety of ways. To this end the containers in practice are often passed through a continuous-heating oven. In general, the powder coatings cure fully at object temperatures between 230 and 350°C within 5 to 30 sec. The continuous-heating oven can be operated at constant temperature or at a temperature profile set to suit the particular circumstances.

The working examples given below elucidate the invention in greater detail. All parts and percentages are by weight, unless expressly stated otherwise. The preparation of the powder coatings was carried out in each case by weighing all components in canisters, premixing them in a premixer, homogenizing the mixture by means of an extruder at 60 to 80°C , cooling it as rapidly as possible and adjusting it to the desired particle size distribution using grinding aggregates.

Example 1

The following components were processed to give powder coating 1:

- | | | |
|----|-----------|--|
| 5 | 500 parts | of a commercial polyester containing a crosslinking catalyst, having an acid value of 35 mg of KOH/g and an OH value of 15 mg of KOH/g (commercial product Grilesta P 7401 from Ems-Chemie), |
| 10 | 248 parts | of a commercial epoxidized novolak resin having an epoxide equivalent weight (EEW) of 700 (commercial product DER 672 U from Dow), |
| 15 | 50 parts | of a commercial epoxy resin based on bisphenol A having an EEW of 800 (commercial product Epikote 3003-4F-10 from Shell Chemie), |
| | 200 parts | of a finely divided silicate filler of the quartz sand type, and |
| 20 | 2 parts | of a fluidization auxiliary agent based on pyrogenic silicic acid. |

Using grinding aggregates, the particle size distribution was adjusted in such a manner that at least 90 % by mass

of the powder coating particles have a particle size between 1 and 25 μm ($d_{90} = 1$ to 25 μm). For at least 99 % by mass of the particles, the maximum particle size is $\leq 100 \mu\text{m}$, the average particle size is about 9 μm . The slope S is 250. This powder coating 1 was applied to a can body (diameter of opening 73 mm, length of body = 110 mm) using suitable equipment, baked for 30 sec. at an object temperature of 280°C and then subjected to an enamel rater test: The coated can was immersed in a Cu/Cd standard solution S475 (conductance $2.2 \pm 0.2 \text{ mS/cm}$) and connected as cathode. A voltage of 6.3 V was applied for a period of 30 sec. and the amperage was measured. The amperage $I = 5 \text{ mA}$ was not exceeded at a film thickness as low as 15 μm . In addition, this powder coating 1 was applied to a tinned can body (deposit of 2.8 mg/m^2) at a film thickness of 15 μm and baked for 30 sec. at an object temperature of 280°C. The coating obtained in this way was subjected to a sterilization test (30 min., 1.6 bar, 128°C) in various test media. Water uptake, (visual) adhesion and flexibility were tested after sterilization. The results are summarized in Table 1.

Table 1: Test results of the powder coating coat 1 (film thickness 15 μm , d 90 = 1-25 μm)

	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	2% lactic acid ⁶⁾
H ₂ O uptake	-	none	none	none	none
Adhesion ¹⁾	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
T-Bend ²⁾	T0	T0	T0	T0	T0

Key to Table 1:

1) adhesion testing by the crosshatch method (DIN 53151)

2) testing by the ECCA (European Coil Coating Association) procedures

3) examination of the untreated coating prior to sterilization

4) test medium = 3% aqueous sodium chloride solution

5) test medium = 3% aqueous acetic acid

6) test medium = 2% aqueous lactic acid

Example 2

Powder coating 2 was prepared in a manner similar to that of Example 1 from the components listed in Example 1. In contrast to Example 1, the particle size distribution was adjusted in such a way that at least 90 % by mass of the powder coating particles have a particle size between 1 and 100 μm ($d_{90} = 1$ to 100 μm). The maximum particle size of at least 99 % by mass of the particles is < 150 μm , the average particle size is about 35 μm . The slope S is 100. This powder coating 2 was applied to a can body (diameter of opening 73 mm, length of body = 110 mm), baked for 30 sec. at an object temperature of 280°C and then subjected to the enamel rater test described in Example 1: A minimum film thickness of 35 μm was required to maintain the amperage $I < 5$ mA.

Furthermore, this powder coating 2 was applied to a tinned (deposit of 2.8 mg/m²) panel (size 20 x 20 cm²) at a film thickness of 80 μm , using suitable spray equipment, and was baked for 30 sec. at an object temperature of 280°C. The coating obtained in this manner was subjected to a sterilization test (30 min., 1.6 bar, 128°C) in various test media. Water uptake (visual), adhesion and flexibility were tested after sterilization. The results are summarized in Table 2.

Table 2: Test results of the powder coating coat 2 (film thickness 80 μm , d 90 = 1-100 μm)

	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	2% lactic acid ⁶⁾
H ₂ O uptake	-	none	none	none	none
Adhesion ¹⁾	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
T-Bend ²⁾	T0	T0	T0	T0	T0

Key to Table 2:

- 1) adhesion testing by the crosshatch method (DIN 53151)
- 2) testing by the ECCA (European Coil Coating Association) procedures
- 3) examination of the untreated coating prior to sterilization
- 4) test medium = 3% aqueous sodium chloride solution
- 5) test medium = 3% aqueous acetic acid
- 6) test medium = 2% aqueous lactic acid

Example 3

The following components were processed to give powder coating 3:

- | | | |
|----|-----------|--|
| 5 | 600 parts | of a commercial polyester containing a crosslinking catalyst, having an acid value of 35 mg of KOH/g and an OH value of 15 mg of KOH/g (commercial product Grilesta P 7401 from Ems-Chemie), |
| 10 | 250 parts | of a commercial epoxy resin based on bisphenol A having an EEW of 600 (commercial product DER 692 from Dow), |
| 15 | 48 parts | of a master batch of 10 parts of a flow control agent based on an oligomeric acrylate in 90 parts of a commercial epoxy resin based on bisphenol A having an EEW of 800 (commercial product E 3003-4F-10 from Shell Chemie), |
| | 100 parts | of a finely divided silicate filler of the quartz sand type, and |
| 20 | 2 parts | of a fluidization agent of the pyrogenic silicic acid type. |

Using grinding aggregates, the particle size distribution was adjusted in such a way that at least 90 % by mass of the powder coating particles have a particle size between 1 and 25 μm ($d_{90} = 1$ to 25 μm). The maximum particle size for at least 99 % by weight of the particles is $\leq 100 \mu\text{m}$, the average particle size is about 11 μm . The slope S is 200.

This powder coating 3 is applied to a can body (diameter of opening 73 mm, length of body = 110 mm) by means of spray aggregates, is baked for 30 sec. at an object temperature of 280°C and then subjected to the enamel rater test described in Example 1: the amperage $I = 5 \text{ mA}$ was not exceeded at a film thickness of less than 15 μm . In addition, this powder coating 3 was applied with the aid of spray aggregates to a tinned can body (deposit of 2.8 mg/m^2) at a film thickness of 15 μm and was baked for 30 sec. at an object temperature of 280°C. The coating obtained in this way was subjected to a sterilization test (30 min., 1.6 bar, 128°C in various test media. Water uptake, adhesion and flexibility were tested after sterilization. The results are summarized in Table 3.

Table 3: Test results of the powder coating coat 3 (film thickness 15 μm , d 90 = 1-25 μm)

	untreat- ed ⁴⁾	H ₂ O	3% NaCl ⁵⁾	3% HAc ⁶⁾	2% lactic acid ⁷⁾
H ₂ O uptake ¹⁾	-	mod.	mod.	strong	strong
Adhesion ²⁾	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
T-Bend ³⁾	T0	T0	T0	T0	T0

Key to Table 3:

(mod. = moderate)

- 1) visual assessment: examination for turbidity or similar
- 2) adhesion testing by the crosshatch method (DIN 53151)
- 3) testing by the ECCA (European Coil Coating Association) procedures
- 4) examination of the untreated coating prior to sterilization
- 5) test medium = 3% aqueous sodium chloride solution
- 6) test medium = 3% aqueous acetic acid
- 7) test medium = 2% aqueous lactic acid

Example 4

Powder coating 4 was prepared in a manner similar to that of Example 3 from the components listed in Example 3. In contrast to Example 3, the particle size distribution was adjusted in such a way that at least 90 % by mass of the powder coating particles have a particle size between 1 and 100 μm ($d_{90} = 1$ to 100 μm). The maximum particle size for at least 99 % by mass of the particles is < 150 μm , the average particle size is about 40 μm . The slope S is 90. This powder coating 4 was applied to a can body (diameter of opening 73 mm, length of body = 110 mm), was baked for 30 sec. at an object temperature of 280°C and then subjected to the enamel rater test described in Example 1: A minimum film thickness of 35 μm was required to maintain the amperage $I < 5$ mA.

In addition, this powder coating 4 was applied to a tinned (deposit of 2.8 mg/m²) panel (size 20 x 20 cm²) at a film thickness of 80 μm and was baked for 30 sec. at an object temperature of 280°C. The coating obtained in this manner was subjected to a sterilization test (30 min., 1.6 bar, 128°C) in various test media. Water uptake (visual), adhesion and flexibility were tested after sterilization. The results are summarized in Table 4.

Table 4: Test results of the powder coating coat 4 (film thickness 80 μm , d 90 = 1-100 μm)

2% (sic)	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	lactic acid ⁶⁾
H ₂ O uptake	-	mod.	mod.	strong	strong
Adhesion ¹⁾	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
T-Bend ²⁾	T2	T2	T2	T3	T3

Key to Table 4:

(mod. = moderate)

- 1) adhesion testing by the crosshatch method (DIN 53151)
- 2) testing by the ECCA (European Coil Coating Association) procedures
- 3) examination of the untreated coat prior to sterilization
- 4) test medium = 3% aqueous sodium chloride solution
- 5) test medium = 3% aqueous acetic acid
- 6) test medium = 2% aqueous lactic acid

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Example 5

Powder coating 5 was prepared from the following components:

5	400 parts	of a commercial polyester containing a crosslinking catalyst, having an acid value of 80 mg of KOH/g, an OH value of about 20 mg of KOH/g, synthesized from terephthalic acid, trimellitic acid, adipic acid, ethylene glycol and neopentyl glycol (commercial product Grilesta V 72-6 from Ems-Chemie),
10	400 parts	of a commercial epoxy resin based on bisphenol A, having an EEW of 750 (commercial product XB 4393 from Ciba Geigy),
15	100 parts	of titanium dioxide of the rutile type,
	93 parts	of a finely divided silicate filler of the quartz sand type,
	5 parts	of a flow control agent based on an oligomeric acrylate, and
20	2 parts	of a fluidization auxiliary agent based on SiO_2 .

Using grinding aggregates, the particle size distribution was adjusted in such a way that at least 90 % by mass of the powder coating particles have a particle size between 5 and 15 μm ($d_{90} = 5$ to 15 μm). The maximum particle size for at least 99 % by mass of the particles is $\leq 100 \mu\text{m}$, the average particle size is about 8 μm . The slope S is 250.

This powder coating 5 was applied to a can body (diameter of opening 73 mm, length of body = 110 mm), was baked for 30 sec. at an object temperature of 280°C and then subjected to the enamel rater test described in Example 1: The amperage $I = 5 \text{ mA}$ was not exceeded at a film thickness of less than 15 μm .

In addition, this powder coating 5 was applied to a tinned can body (deposit of 2.8 mg/m^2) at a film thickness of 15 μm and was baked for 30 sec. at an object temperature of 280°C. The coating obtained in this manner was subjected to a sterilization test (30 min., 1.6 bar, 128°C) in various test media. Water uptake (visual), adhesion and flexibility were tested after sterilization. The results are summarized in Table 5.

Table 5: Test results of the powder coating coat 5 (film thickness 15 μm , d 90 = 5-15 μm)

	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	2% lactic acid ⁶⁾
H ₂ O uptake	-	none	none	none	none
Adhesion ¹⁾	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
T-Bend ²⁾	T0	T0	T0	T0	T0

Key to Table 5:

- 1) adhesion testing by the crosshatch method (DIN 53153)
- 2) testing by the ECCA (European Coil Coating Association) procedures
- 3) examination of the untreated coat prior to sterilization
- 4) test medium = 3% aqueous sodium chloride solution
- 5) test medium = 3% aqueous acetic acid
- 6) test medium = 2% aqueous lactic acid

Example 6

Powder coating 6 was prepared in a manner similar to that of Example 5 from the components listed in Example 5. In contrast to Example 5, the particle size distribution was adjusted in such a way that at least 90 % by mass of the powder coating particles have a particle size between 1 and 100 μm ($d_{90} = 1$ to 100 μm). The maximum particle size for at least 99 % by mass of the particles is $\leq 150 \mu\text{m}$, the mean particle size is about 40 μm . The slope S is 100. This powder coating 6 was applied to a can body (diameter of opening 73 mm, length of body = 110 mm), was baked for 30 sec. at 280°C and then subjected to the enamel rater test described in Example 1: A minimum film thickness of 25 μm is required to maintain the amperage $I < 5 \text{ mA}$.

In addition, this powder coating 6 was applied to a tinned (deposit of 2.8 mg/m²) panel (size 20 x 20 cm²) at a film thickness of 80 μm and was baked for 30 sec. at an object temperature of 280°C. The coating obtained in this manner was subjected to a sterilization test (30 min., 1.6 bar, 128°C) in various test media. Water uptake (visual), adhesion and flexibility were tested after sterilization. The results are summarized in Table 6.

Table 6: Test results of the powder coating coat 6 (film thickness 80 μm , d 90 = 1-100 μm)

	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	2% lactic acid ⁶⁾
H ₂ O uptake	-	none	none	none	none
Adhesion ¹⁾	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
T-Bend ²⁾	T0	T0	T0	T0	T0

Key to Table 6:

- 1) adhesion testing by the crosshatch method (DIN 53151)
- 2) testing by the ECCA (European Coil Coating Association) procedures
- 3) examination of the untreated coating prior to sterilization
- 4) test medium = 3% aqueous sodium chloride solution
- 5) test medium = 3% aqueous acetic acid
- 6) test medium = 2% aqueous lactic acid

In addition, pack tests were carried out on cans whose weld seams were coated with powder coating 6 (application by means of suitable spray aggregates, curing for 30 sec. at an object temperature of 280°C, film thickness 60 - 80 μm , coating of the can interiors with a conventional, commercial spray paint). The foodstuff cans

were filled with water, 3% acetic acid and 2% lactic acid and sealed. The cans were sterilized for 30 min. at 1.6 bar and 128°C and then stored at 37°C.

5 No damage to the coating was apparent after 6 months' storage.

Example 7

The following components were processed to give powder coating 7:

10	425 parts	of a commercial polyester containing an esterification catalyst, having an acid value of 80 mg of KOH/g and an OH value of 20 mg of KOH/g (commercial product Grilesta V 72-6 from Ems-Chemie),
15	475 parts	of a commercial epoxy resin based on bisphenol A, having an EEW of 800 (commercial product XZ 86795 from Dow),
	50 parts	of talc,
20	48 parts	of a masterbatch of 10 parts of a flow control agent based on an oligomeric acrylate in 90 parts of the abovementioned commercial polyester having an acid value of 80 mg of KOH/g and an OH value of 20 mg

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of KOH/g, and

2 parts of a fluidization auxiliary agent based on pyrogenic silicic acid.

Using gridding aggregates, the particle distribution was
5 adjusted in such a way that 90 % by mass of the powder
coating particles have a particle size between 1 and
25 μm ($d_{90} = 1$ to 25 μm). The maximum particle size for
at least 99 % by mass of the particles is $\leq 100 \mu\text{m}$, the
average particle size is about 14 μm . The slope S is
10 200. This powder coating 7 was applied to a can body
(diameter of opening 73 mm, length of body = 110 mm),
baked for 30 sec. at an object temperature of 280°C and
then subjected to the enamel rater test described in
Example 1: A minimum film thickness of 15 μm is required
15 to maintain an amperage $I < 5 \text{ mA}$.

In addition, this powder coating 7 was applied to a
tinned (deposit of 2.3 mg/m^2) panel (size 20 x 20 cm^2) at
a film thickness of 30 μm and baked for 30 sec. at an
object temperature of 280°C. The coating obtained in this
20 manner was subjected to a sterilization test (30 min.,
1.6 bar, 128°C) in various test media. Water uptake
(visual), adhesion and flexibility were tested after
sterilization. The results are summarized in Table 7.

Table 7: Test results of the powder coating coat 7 (film thickness 30 μm , d 90 = 1-25 μm)

	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	2% lactic acid ⁶⁾
H ₂ O uptake	-	strong	strong	strong	strong
Adhesion ¹⁾	Gt 0	Gt 0	Gt 2	Gt 0	Gt 2
T-Bend ²⁾	T0	T0	T0	T0	T0

Key to Table 7:

- 1) adhesion testing by the crosshatch method (DIN 53151)
- 2) testing by the ECCA (European Coil Coating Association) procedures
- 3) examination of the untreated coating prior to sterilization
- 4) test medium = 3% aqueous sodium chloride solution
- 5) test medium = 3% aqueous acetic acid
- 6) test medium = 2% aqueous lactic acid

Example 8

Powder coating 8 was prepared in a manner similar to that of Example 7 from the components listed in Example 7. In contrast to Examl 7, the particle size distribution was adjusted in such a way that at least 90 % by mass of the

- powder coating particles have a particle size between 1 and 100 μm ($d_{90} = 1$ to 100 μm). The maximum particle size for at least 99 % by mass of the particles is $\leq 150 \mu\text{m}$, the average particle size is about 35 μm . The slope S is
- 5 150. This powder coating 8 was applied to a can body (diameter of opening 73 mm, length of body = 110 mm), baked for 30 sec. at an object temperature of 280°C and then subjected to the enamel rater test. A minimum film thickness of 35 μm is required to maintain the amperage $I < 5 \text{ mA}$.
- 10 In addition, this powder coating 8 was applied to a tinned (deposit of 2.8 mg/m^2) panel (size 20 x 20 cm^2) at a film thickness of 80 μm and baked for 30 sec. at an object temperature of 280°C. The coating obtained in this manner was subjected to a sterilization test
- 15 (30 min., 1.6 bar, 128°C) in various test media. Water uptake (visual), adhesion and flexibility were tested after sterilization. The results are summarized in Table 8.

Table 8: Test results of the powder coating coat 8 (film thickness 80 μm , d 90 = 1-100 μm)

	untreat- ed ³⁾	H ₂ O	3% NaCl ⁴⁾	3% HAc ⁵⁾	2% lactic acid ⁶⁾
H ₂ O uptake	-	strong	strong	strong	strong
Adhesion ¹⁾	Gt 0	Gt 0	Gt 2	Gt 0	Gt 2
T-Bend ²⁾	T2	T2	T3	T3	T4

Key to Table 8:

- 1) adhesion testing by the crosshatch method (DIN 53151)
- 2) testing by the ECCA (European Coil Coating Association) procedures
- 3) examination of the untreated coating prior to sterilization
- 4) test medium = 3% aqueous sodium chloride solution
- 5) test medium = 3% aqueous acetic acid
- 6) test medium = 2% aqueous lactic acid

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Patent claims

1. A powder coating for the coating of packaging container interiors, based on epoxy resins and carboxyl-containing polyesters, wherein

5 1) the powder coating contains

A) at least one polyester having an acid value of 25 to 120 mg of KOH/g and an OH value > 10 mg of KOH/g and

10 B) at least one epoxy resin having an epoxide equivalent weight of 400 to 3000, and

2) the powder coating has such a particle size distribution that

15 a) at least 90% by mass of the powder coating particles have a particle size between 1 and 60 μm ,

b) the maximum particle size for at least 99% by mass of the powder coating particles is $\leq 100 \mu\text{m}$,

20 c) the average particle size of the powder coating particles is between 5 and 20 μm , and

d) the slope of the particle distribution curve
at the inflection point is ≥ 100 .

2. The powder coating as claimed in claim 1, which has
such a particle size distribution that

5 a) at least 90% by mass of the powder coating
particles have a particle size between 1 and
40 μm ,

b) the maximum particle size of the powder coating
particles for at least 99 % by mass of the
10 particles is $\leq 60 \mu\text{m}$,

c) the average particle size of the powder coating
particles is between 5 and 12 μm , and

d) the slope of the particle distribution curve at
the inflection point is ≥ 150 .

15 3. The powder coating as claimed in claim 1, which has
such a particle size distribution that

a) at least 90 % by mass of the powder coating
particles have a particle size between 5 and
25 μm ,

20 b) the maximum particle size of the powder coating
particles for at least 99 % by mass of the

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particles is $\leq 40 \mu\text{m}$,

- c) the average particle size of the powder coating particles is between 5 and 12 μm , and
- d) the slope of the particle distribution curve at the inflection point is ≥ 200 .

4. The powder coating as claimed in claim 1, which contains

- A) at least one polyester having an acid value of 30 to 90 mg of KOH/g and an OH value of 15 to 30 mg of KOH/g, and
- B) at least one epoxy resin having an epoxide equivalent weight of 600 to 900.

5. The powder coating as claimed in 1, which contains, as component B, an epoxy resin based on bisphenol A or an epoxidized novolak resin.

6. The powder coating as claimed in claim 1, which contains, as component A, a polyester based on terephthalic or trimellitic acid and ethylene glycol or neopentyl glycol.

7. The powder coating as claimed in claim 1, wherein the powder coating contains

- A) 19 to 80 % by weight, based on the total weight of the powder coating, the polyester component A and
- B) 19 to 80 % by weight, based on the total weight of the powder coating, of the epoxy resin component B.

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8. A process for the coating of packaging container interiors, wherein a powder coating as claimed in any one of claims 1 to 7 is applied at a film thickness of $< 15 \mu\text{m}$.

9. A process for the coating of packaging container weld seams, wherein a powder coating as claimed in any one of claims 4 to 7 is applied.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS

